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Rich nitrogen atoms in an azine covalent organic framework for gas uptake

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Experimental

Materials

Acetic acid, tetrahydrofuran, n-butanol, o-DCB, DMF, and other chemicals were obtained from J&K Scientific company, TCI, Wako, and Sigma-Aldrich.

Material Characterization

Recording Fourier Transform Infrared (FT-IR) Spectrum with FT-IR Frontier Infrared Spectrometer with Perkin-Elmer Model. For all FT-IR tests, a small amount of sample can be directly mixed with potassium bromide and ground into a powder, compressed, Photoluminescence spectra were recorded on JASCO model FP-8600 spectrofluorometer. Elemental analysis (C, H, and N) was performed on a Euro Vector EA3000 elemental analyzer. Solid-state ^{13}C CP/MAS NMR measurements were recorded using a Bruker AVANCE III 400 WB spectrometer at a MAS rate of 5 kHz and a CP contact time of 2 ms. Field-emission scanning electron microscopy (FE-SEM) images were performed on a JEOL model JSM-6700 operating at an accelerating voltage of 5.0 kV. The samples were prepared for SEM by drop-casting a tetrahydrofuran suspension onto mica substrate and then coated with gold. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from $2\theta = 1.5°$ up to 30° with 0.02° increment. TGA analysis was carried out using a Q5000IR analyser (TA Instruments) with an automated vertical overhead thermobalance. Before measurement, the samples were heated at a rate of 5 °C min^{-1} under a nitrogen atmosphere. Nitrogen sorption isotherms were measured at 77 K with ASIQ (iQ-2) volumetric adsorption analyzer. Before measurement, the samples were degassed in vacuum at 150 °C for more than 10h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas and pore volume. The nonlocal density functional theory (NLDFT) method was applied for the estimation of pore size and pore size distribution.

Synthesis of Ns-COF

A pyrex tube is charged with 40 mg (0.10 mmol) of TFPT, hydrazine hydrate (9.3 μL, 80% 0.15 mmol), 0.5 mL of o-DCB, 1.5 mL of n-BuOH, and 0.2 mL of 6 M aqueous acetic acid. The reaction mixture was heated at 120 °C for 3 days. Slow cooling to room temperature the tube was opened and the whole mixture was centrifuged (3 x 5 min, 9000 rpm) while being

washed with acetone (3 x 7 mL) and THF (2 x 7 mL). And then dried at 120 °C under vacuum for 24 hours to give a light yellow colored powder. (41.7mg, yield 88%)

Iodine sorption

Three open vials (5 mL) with COFs samples were kept in a large bottle (70 mL) containing iodine (3.0 g). The large bottle was sealed and stored at 350 K. Three open vials were cooled down to room temperature and weighted to observe iodine capture value by the selected time. The large vial was restored at 350 K to observe iodine capture. The COF loading the iodine in ethanol were stirred for 3 hours. The samples were obtained via the filter operation, and further washed with ethanol for five times to take off iodine of COFs. This process was performed five times. Finally, the regenerated COFs were dried at 100 ℃ under a vacuum for the next experiment. Each experiment was done for three times.

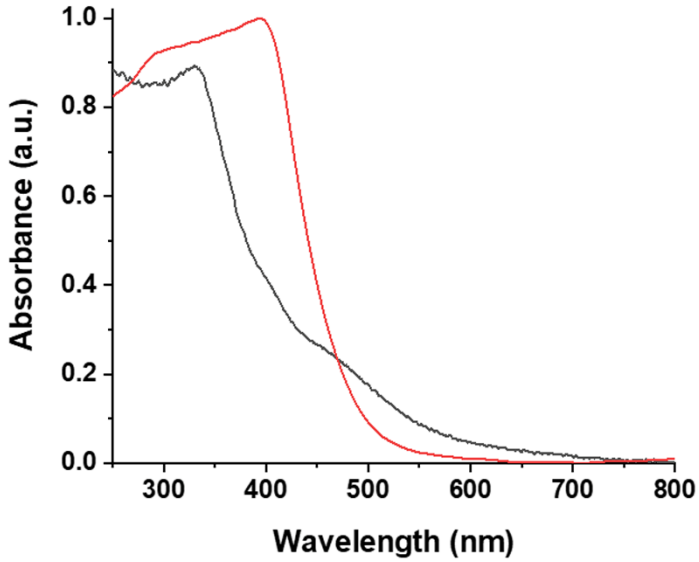

Fig. S1. Solid-state electronic absorption spectra of TFPT (black) and Ns-COF (red)

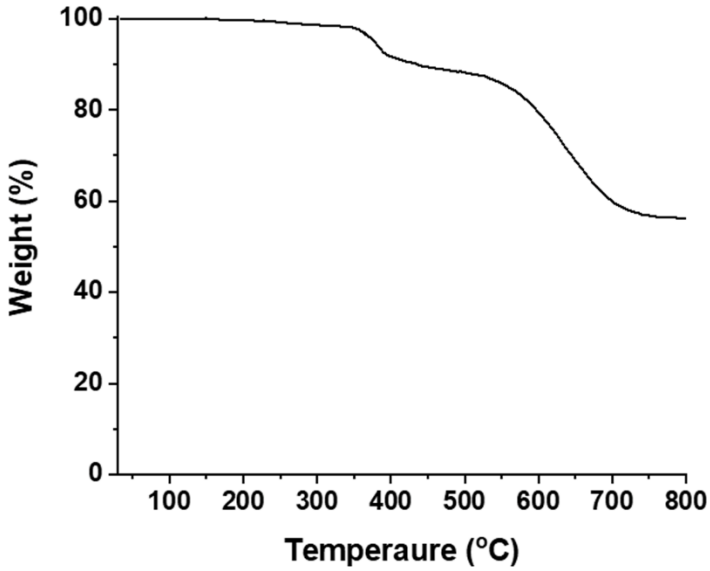

Fig. S2. TGA curve of Ns-COF under nitrogen atmosphere.

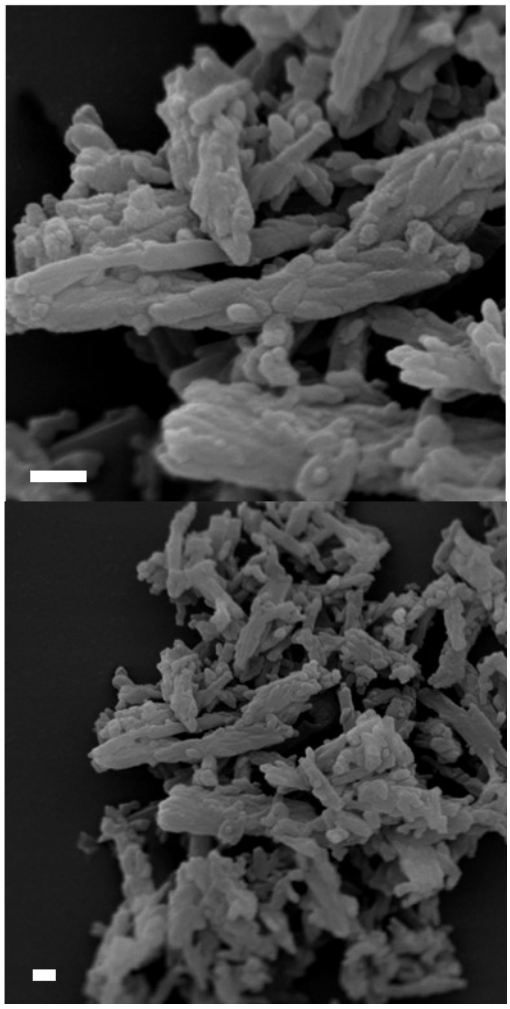

Fig. S3. Field-emission scanning electron microscopy image of Ns-COF (scale bar: 1 μm).

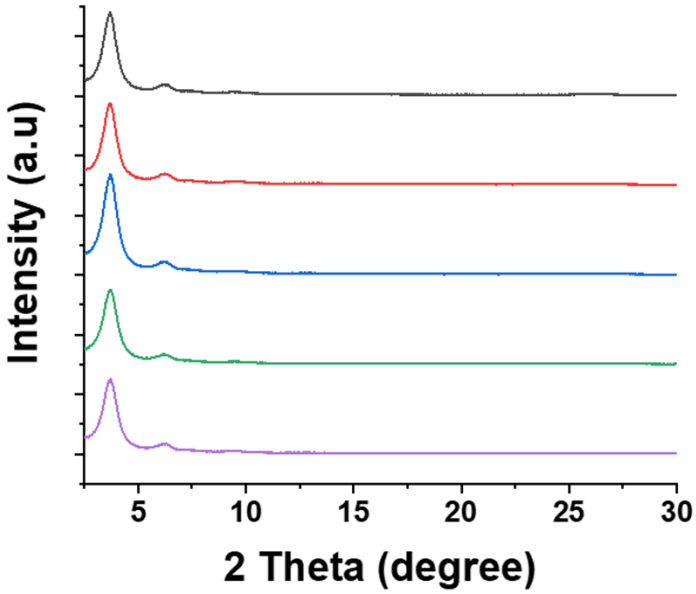

Fig. S4. PXRD patterns of Ns-COFs. (black: as-synthesis; red: hexane; blue: water; green; 0.1 M HCl; purple: 0.1 M NaOH).

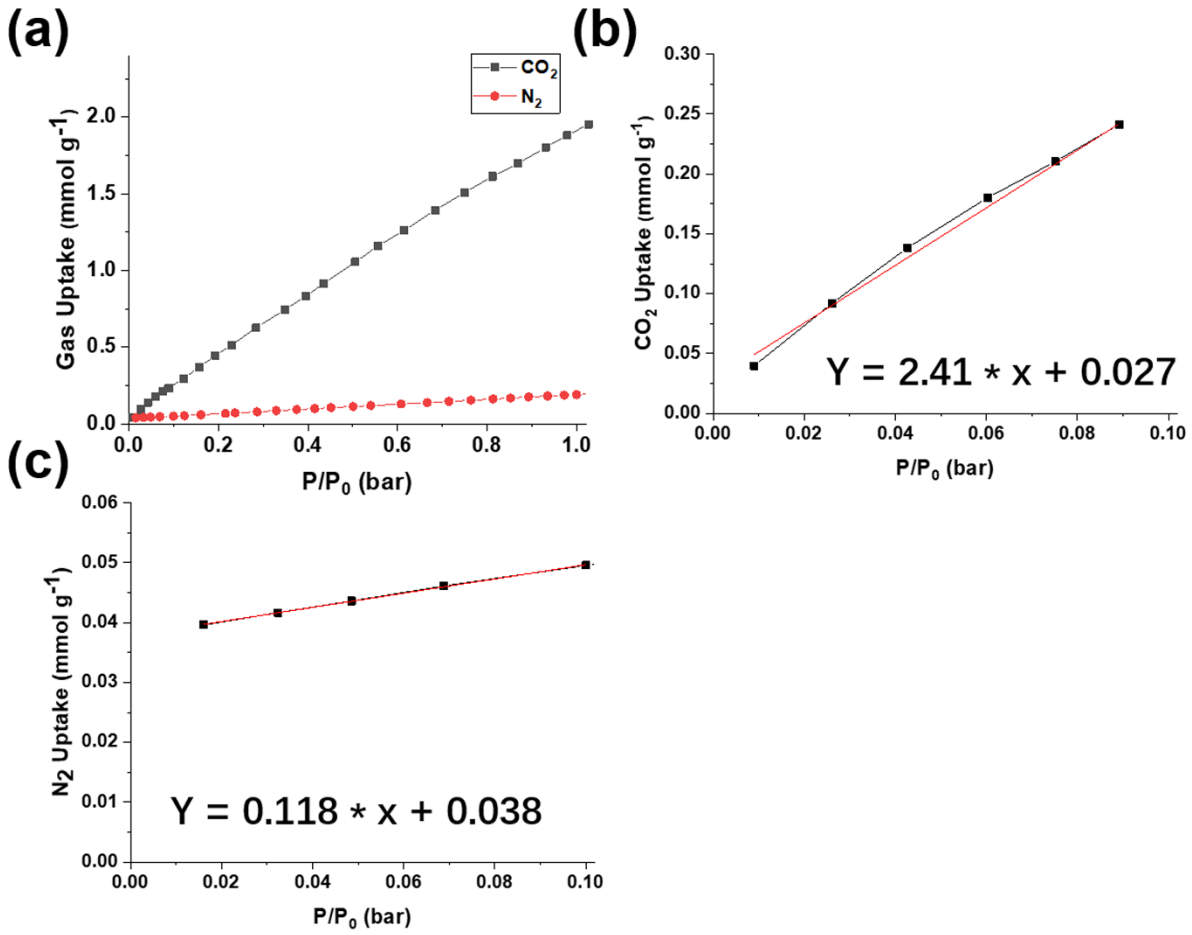

Fig. S5. Gas uptake of Ns-COF.

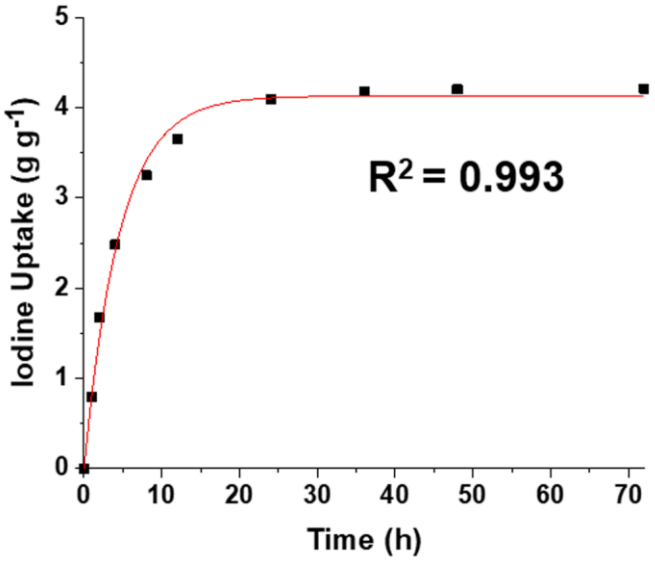

Fig. S6. The kinetic of iodine adsorption via the pseudo-first-order kinetic model.

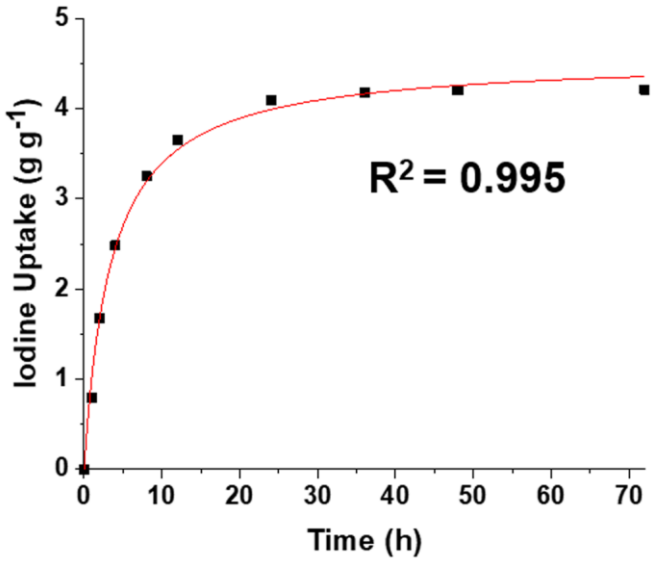

Fig. S7. The kinetic of iodine adsorption via the pseudo-second-order kinetic model.

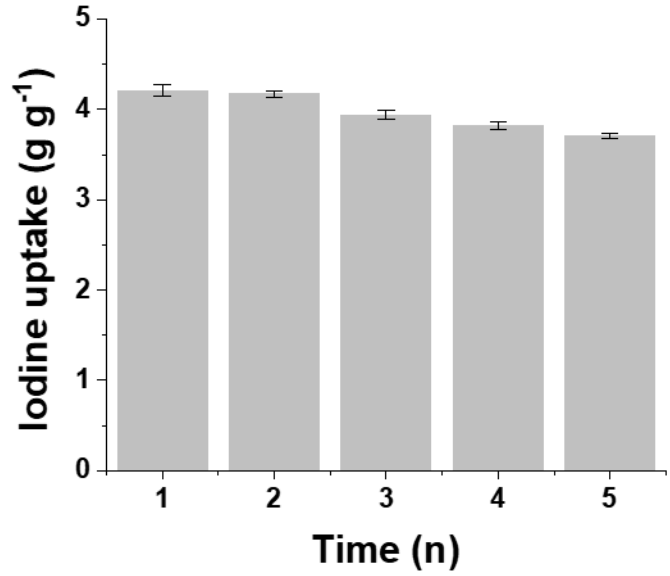

Fig. S8. Recycle experiment of Ns-COF for iodine capture.

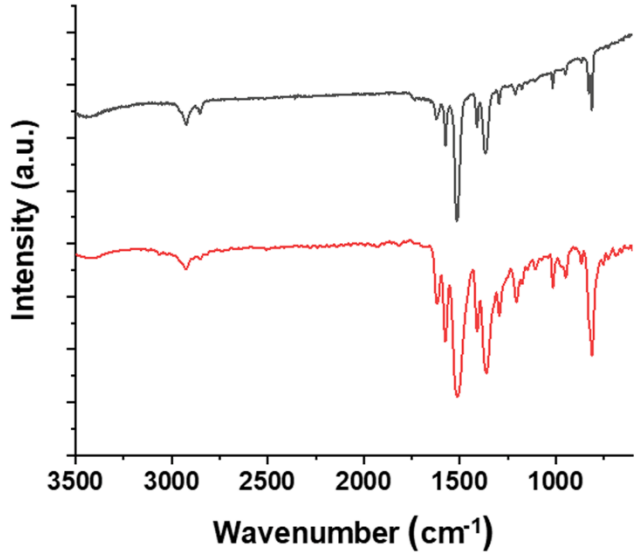

Fig. S9. FT-IR spectra of Ns-COF (black) and re-used Ns-COF (red).

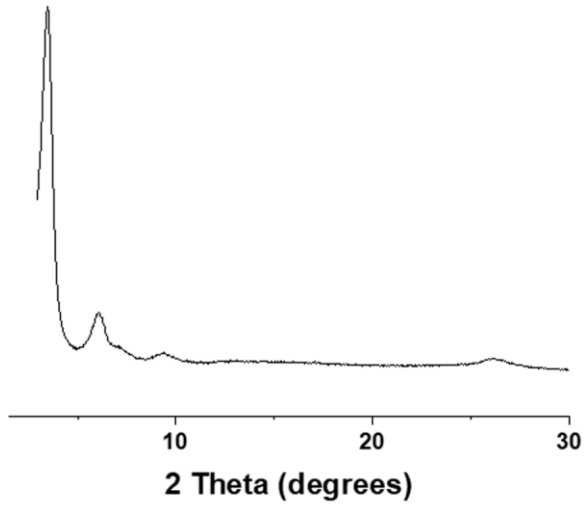

Fig. S10. PXRD patterns of re-used Ns-COF.